

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
18 September 2003 (18.09.2003)

PCT

(10) International Publication Number  
**WO 03/076692 A1**

(51) International Patent Classification<sup>7</sup>: C25C 5/00, C22B 9/14, 34/12

(21) International Application Number: PCT/AU03/00305

(22) International Filing Date: 13 March 2003 (13.03.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
PS 1170 13 March 2002 (13.03.2002) AU

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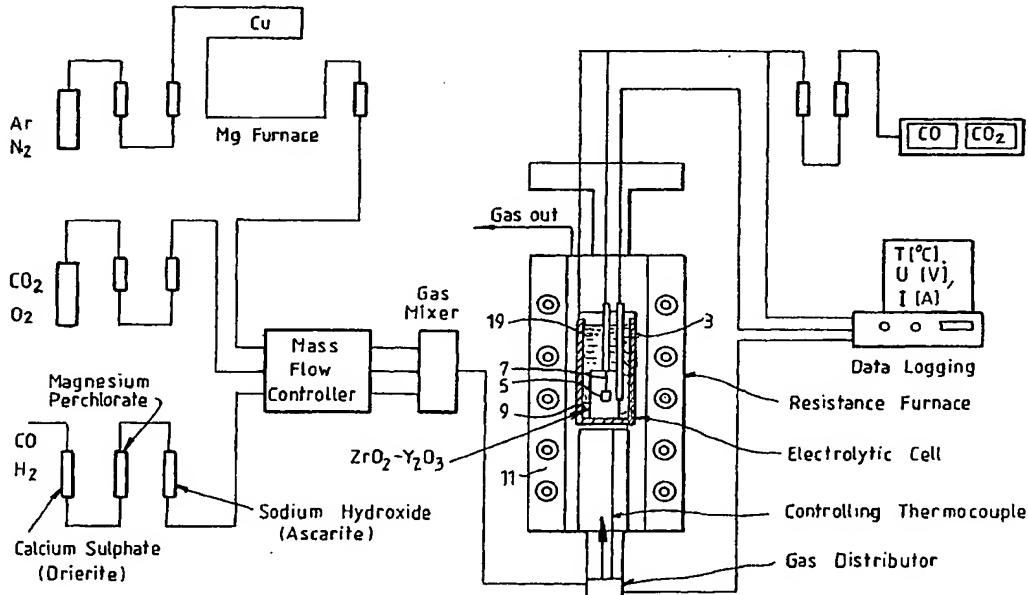
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(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BR, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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(54) Title: MINIMISING CARBON TRANSFER IN AN ELECTROLYTIC CELL



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(57) Abstract: An electrolytic cell for reducing a metal oxide, such as titania, in a solid state is disclosed. The electrolytic cell includes an anode formed from carbon and a cathode formed at least in part from the metal oxide. The electrolytic cell also includes a membrane that is permeable to oxygen anions and is impermeable to carbon in ionic and non-ionic forms positioned between the cathode and the anode to thereby prevent migration of carbon to the cathode.

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**Published:**

— *with international search report*

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## MINIMISING CARBON TRANSFER IN AN ELECTROLYTIC CELL

The present invention relates to reduction of metal oxides in a solid state in an electrolytic cell.

5

The present invention was made during the course of an on-going research project on solid state reduction of titania ( $TiO_2$ ) carried out by the applicant.

10

During the course of the research project the applicant carried out experimental work on the reduction of titania using an electrolytic cell that included a graphite crucible that formed an anode of the cell, a pool of molten  $CaCl_2$ -based electrolyte in the crucible, and a range of cathodes that included solid titania.

15

The  $CaCl_2$ -based electrolyte was a commercially available source of  $CaCl_2$ , namely calcium chloride dihydrate, that partially decomposed on heating and produced  $CaO$ .

20

The applicant operated the electrolytic cell at a potential above the decomposition potential of  $CaO$  and below the decomposition potential of  $CaCl_2$ .

25

The applicant found that the cell could electrochemically reduce titania to titanium with very low concentrations of oxygen.

30

The applicant does not have a clear understanding of the electrolytic cell mechanism at this stage. Nevertheless, whilst not wishing to be bound by the comments in this and the following paragraphs, the applicant offers the following comments by way of an outline of a possible cell mechanism.

The experimental work carried out by the

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applicant produced evidence of Ca metal dissolved in the electrolyte. The applicant believes that, at least during the early stages of operation of the cell, the Ca metal was the result of electrodeposition of  $\text{Ca}^{++}$  cations as Ca metal on electrically conductive sections of the cathode.

The experimental work was carried out using a  $\text{CaCl}_2$ -based electrolyte at a cell potential below the decomposition potential of  $\text{CaCl}_2$ . The applicant believes that the initial deposition of Ca metal on the cathode was due to the presence of  $\text{Ca}^{++}$  cations and  $\text{O}^{--}$  anions derived from  $\text{CaO}$  in the electrolyte. The decomposition potential of  $\text{CaO}$  is less than the decomposition potential of  $\text{CaCl}_2$ . In this cell mechanism the cell operation is dependent, at least during the early stages of cell operation, on decomposition of  $\text{CaO}$ , with  $\text{Ca}^{++}$  cations migrating to the cathode and depositing as Ca metal and  $\text{O}^{--}$  anions migrating to the anode and forming  $\text{CO}$  and/or  $\text{CO}_2$  (in a situation in which the anode is a graphite anode).

20

The applicant believes that the Ca metal that deposited on electrically conductive sections of the cathode was deposited predominantly as a separate phase in the early stages of cell operation and thereafter dissolved in the electrolyte and migrated to the vicinity of the titania in the cathode and participated in chemical reduction of titania.

30 The applicant also believes that at later stages of the cell operation part of the Ca metal that deposited on the cathode was deposited directly on partially deoxidised titanium and thereafter participated in chemical reduction of titanium.

35 The applicant also believes that the  $\text{O}^{--}$  anions, once extracted from the titania, migrated to the anode and reacted with anode carbon and produced  $\text{CO}$  and/or  $\text{CO}_2$  (and

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in some instances CaO) and released electrons that facilitated electrolytic deposition of Ca metal on the cathode.

5        However, notwithstanding that the cell could electrochemically reduce titania to titanium with very low concentrations of oxygen, the applicant also found that there were relatively significant amounts of carbon transferred from the anode to the electrolyte and to the  
10      titanium produced at the cathode under a wide range of cell operating conditions.

15      Carbon in the titanium is an undesirable contaminant. In addition, carbon transfer was partially responsible for low energy efficiency of the cell. Both problems are significant barriers to commercialisation of electrolytic reduction technology.

20      The applicant carried out experimental work to identify the mechanism for carbon transfer and to determine how to minimise carbon transfer and/or to minimise the adverse effects of carbon transfer.

25      The experimental work indicated that the mechanism of carbon transfer is electrochemical rather than erosion and that one way of minimising carbon transfer and therefore contamination of titanium produced at the cathode by electrochemical reduction of titania at the cathode is to position a membrane that is permeable to oxygen anions and is impermeable to carbon in ionic and non-ionic forms between the cathode and the anode and thereby prevent migration of carbon to the cathode.

35      Accordingly, the present invention provides an electrolytic cell for reducing a metal oxide in a solid state, which electrolytic cell includes an anode formed from carbon, a cathode formed at least in part from the

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metal oxide, and a membrane that is permeable to oxygen anions and is impermeable to carbon in ionic and non-ionic forms positioned between the cathode and the anode to thereby prevent migration of carbon to the cathode.

5

Preferably, the anode is formed from graphite.

The membrane may be formed from any suitable material.

10

Preferably, the membrane is formed from a solid electrolyte.

15

One suitable solid electrolyte tested by the applicant is yttria stabilised zirconia.

Preferably, the cathode also includes an electrical conductor.

20

The present invention also provides a method of reducing a metal oxide in a solid state using the above-described electrolytic cell.

25

Preferably, the method includes a step of operating the cell at a potential that is above a decomposition potential of at least one of the constituents of the electrolyte so that there are cations of a metal other than that of the metal oxide in the electrolyte.

30

In a situation in which the metal oxide is a titanium oxide, such as titania, it is preferred that the electrolyte be a  $\text{CaCl}_2$ -based electrolyte that includes  $\text{CaO}$  as one of constituents.

35

In such a situation it is preferred that the cell potential be above the decomposition potential for  $\text{CaO}$ .

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It is also preferred that the cell potential be below the decomposition potential for  $\text{CaCl}_2$ .

5 It is preferred that the cell potential be less than or equal to 3.0 V.

It is preferred particularly that the cell potential be below 2.5 V.

10 It is preferred more particularly that the cell potential be below 2.0 V.

15 It is preferred that the cell potential be above 1.5 V.

20 The  $\text{CaCl}_2$ -based electrolyte may be a commercially available source of  $\text{CaCl}_2$ , such as calcium chloride dihydrate, that partially decomposes on heating and produces  $\text{CaO}$  or otherwise includes  $\text{CaO}$ .

25 Alternatively, or in addition, the  $\text{CaCl}_2$ -based electrolyte may include  $\text{CaCl}_2$  and  $\text{CaO}$  that are added separately or pre-mixed to form the electrolyte.

30 The present invention is described further with reference to the following Example that relates to experimental work on the above-described electrolytic cell.

35 As indicated above, the cell included a high density graphite crucible that formed the anode of the cell, a pool of molten  $\text{CaCl}_2$  electrolyte in the crucible, and a cathode that included solid titania. In the initial experimental set-up the solid titania was in the form of titania pellets connected to a lower end of a Kanthal or stainless steel electrically conductive wire.

5 As indicated above, experimental work on the cell identified carbon transfer as a significant issue in terms of contamination of cathode titanium and causing low energy efficiency of the cell. In addition, as indicated above, the experimental work established that carbon transfer was caused by an electrochemical reaction at the anode.

10 Thereafter the applicant carried out experimental work to investigate whether it was possible to prevent migration of carbon from the anode to the cathode.

15 One experiment investigated the impact of a solid ionic barrier on carbon migration.

20 The ionic barrier was in the form of a yttria stabilised zirconia membrane positioned between the anode and the cathode, thereby dividing the cell into an outer anode chamber and an inner cathode chamber.

25 Figure 1 is a schematic of the cell set-up for the experiment. With reference to the Figure, the cell included a graphite crucible 3 that formed the anode, a pool 19 of molten  $\text{CaCl}_2$  electrolyte in the crucible, titania pellets 5 and an electrically conductive wire 7 that formed the cathode immersed in the electrolyte, and a yttria stabilised zirconia membrane 9 immersed in the electrolyte between the anode and the cathode. The cell 30 was located in a resistance furnace 11 heated to a temperature to maintain the electrolyte in a molten state. The experimental set-up also included gas monitoring, cleaning, and analysis equipment. The cell was operated at an applied potential of 3V for a period of 35 hours, 35 during which time there was continuous monitoring of the off-gas from the furnace. At the conclusion of the experiment, the cell was cooled and the solidified

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electrolyte, the membrane, the anode and the cathode were analysed.

5 Figure 2 is a summary of the results of the experiment.

Figure 2 shows measured voltage, current, CO and CO<sub>2</sub> composition of the off-gas for the experiment.

10 Visual and analytical examination of the cathode and the cathode chamber indicated that there was no carbon on the cathode and in the cathode chamber.

15 In addition, the visual and analytical examination of the cathode indicated that titania was reduced to titanium. It follows from this finding that the yttria stabilised zirconia membrane did not restrict migration of O<sup>2-</sup> anions from the cathode to the anode.

20 Many modifications may be made to the present invention as described above without departing from the spirit and scope of the invention.

25 By way of example, whilst the above description of the invention focuses on reduction of titania, the invention is not so limited and extends to electrolytic reduction of other titanium oxides and to oxides of other metals and alloys.

30 Examples of other potentially important metals are aluminium, silicon, germanium, hafnium, magnesium, and molybdenum.

35 Furthermore, whilst the above description focuses on CaCl<sub>2</sub>-based electrolyte, the invention is not so limited and extends to any other suitable electrolytes.

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Generally, suitable electrolytes will be salts and oxides that are soluble in salts. One example of a potentially suitable electrolyte is BaCl<sub>2</sub>.

## CLAIMS:

1. An electrolytic cell for reducing a metal oxide in a solid state, which electrolytic cell includes an anode formed from carbon, a cathode formed at least in part from the metal oxide, and a membrane that is permeable to oxygen anions and is impermeable to carbon in ionic and non-ionic forms positioned between the cathode and the anode to thereby prevent migration of carbon to the cathode.
2. The cell defined in claim 1 wherein the anode is formed from graphite.
- 15 3. The cell defined in claim 1 or claim 2 wherein the membrane is formed from a solid electrolyte.
4. The cell defined in claim 3 wherein the solid electrolyte is yttria stabilised zirconia.
- 20 5. The cell defined in any one of the preceding claims wherein the cathode also includes an electrical conductor.
- 25 6. A method of reducing a metal oxide in a solid state using an electrolytic cell that includes an anode formed from carbon, a cathode formed at least in part from the metal oxide, and a membrane that is permeable to oxygen anions and is impermeable to carbon in ionic and 30 non-ionic forms positioned between the cathode and the anode to thereby prevent migration of carbon to the cathode, which method includes operating the cell at a potential that electrolytically reduces the metal oxide.
- 35 7. The method defined in claim 6 includes operating the cell at a potential that is above a decomposition potential of at least one of the constituents of the

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electrolyte so that there are cations of a metal other than that of the metal oxide in the electrolyte.

8. The method defined in claim 6 or claim 7 wherein  
5 the metal oxide is a titanium oxide, such as titania and  
the electrolyte is a  $\text{CaCl}_2$ -based electrolyte that includes  
CaO as one of constituents.

9. The method defined in claim 8 includes operating  
10 the cell at a potential that is above the decomposition  
potential for CaO.

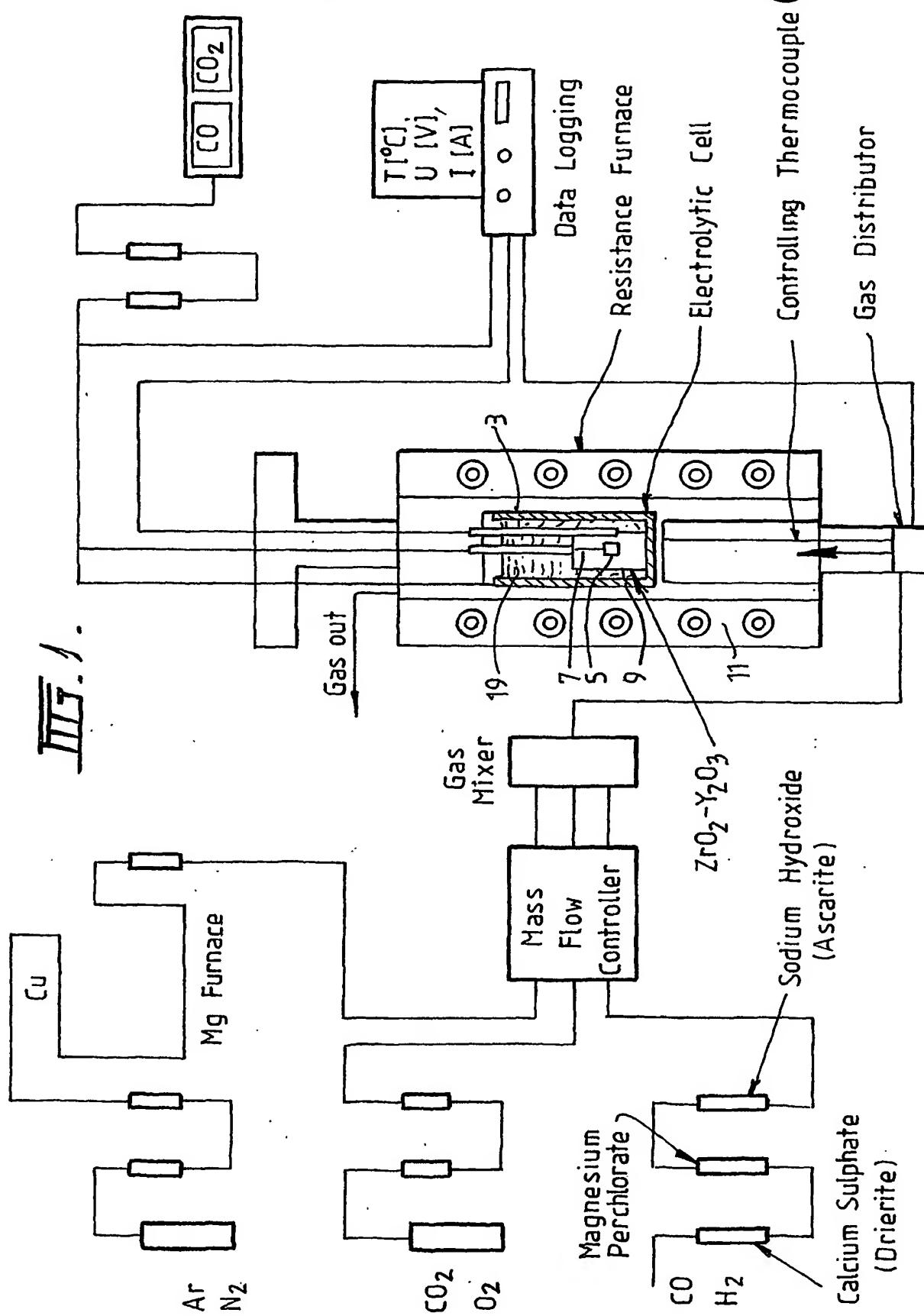
10. The method defined in claim 8 or claim 9 includes  
operating the cell at a potential that is below the  
15 decomposition potential for  $\text{CaCl}_2$ .

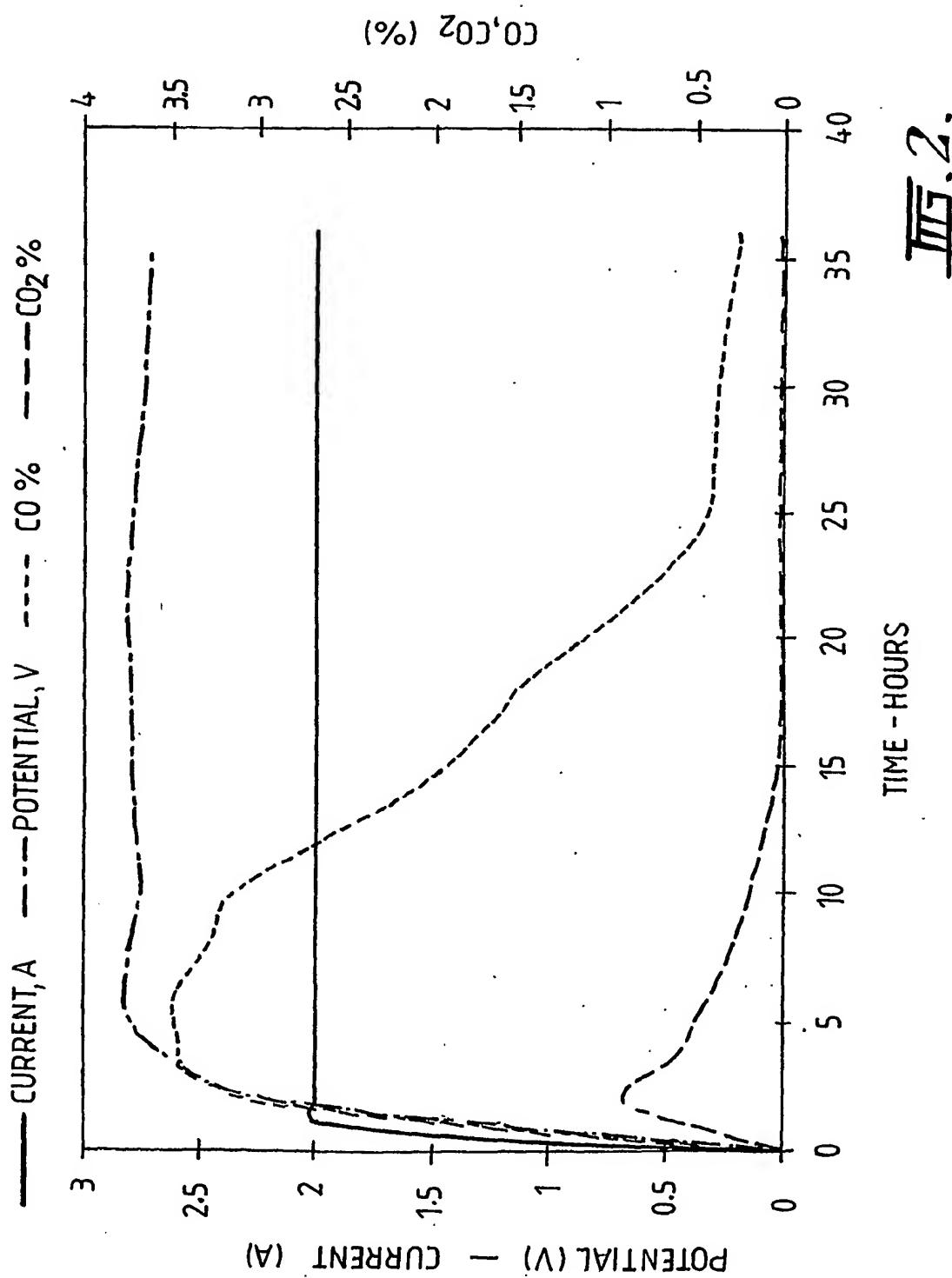
11. The method defined in any one of claims 6 to 10  
wherein the cell potential is less than or equal to 3.0 V.

20 12. The method defined in claim 11 wherein the cell  
potential is below 2.5 V.

13. The method defined in claim 12 wherein the cell  
potential is below 2.0 V.

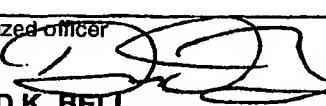
25 14. The method defined in any one of claims 6 to 13  
wherein the cell potential is above 1.5 V.





## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/AU03/00305

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|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>A. CLASSIFICATION OF SUBJECT MATTER</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                                                                                                                                                              |
| Int. Cl. <sup>7</sup> : C25C 5/00, C22B 9/14, 34/12                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                                                                                                                                                              |
| According to International Patent Classification (IPC) or to both national classification and IPC                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                                                                                                                                              |
| <b>B. FIELDS SEARCHED</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |                                                                                                                                                              |
| Minimum documentation searched (classification system followed by classification symbols)<br><b>IPC<sup>7</sup> AS ABOVE</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                                                                                                                                              |
| Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                                                                                                              |
| Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)<br>Derwent WPI: IPC as above and electrol+                                                                                                                                                                                                                                                                                                                                                                                                                                                |                                                                                                                                                              |
| <b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                                                                                                              |
| Category*                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | Citation of document, with indication, where appropriate, of the relevant passages                                                                           |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | WO 9964638 A1 (Cambridge University) 16 December 1999<br>Whole Document                                                                                      |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | GB 2359564 A (Secretary of State for Defence UK) 29 August 2001<br>Whole Document                                                                            |
| <input type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |                                                                                                                                                              |
| * Special categories of cited documents:<br>"A" document defining the general state of the art which is not considered to be of particular relevance<br>"E" earlier application or patent but published on or after the international filing date<br>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)<br>"O" document referring to an oral disclosure, use, exhibition or other means<br>"P" document published prior to the international filing date but later than the priority date claimed |                                                                                                                                                              |
| Date of the actual completion of the international search<br>10 April 2003                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             | Date of mailing of the international search report<br>24 APR 2003                                                                                            |
| Name and mailing address of the ISA/AU<br>AUSTRALIAN PATENT OFFICE<br>PO BOX 200, WODEN ACT 2606, AUSTRALIA<br>E-mail address: pct@ipaaustralia.gov.au<br>Facsimile No. (02) 6285 3929                                                                                                                                                                                                                                                                                                                                                                                                                                 | Authorized officer<br><br>DAVID K. BELL<br>Telephone No : (02) 6283 2309 |

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/AU03/00305

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

| Patent Document Cited in Search Report |         | Patent Family Member |           |    |           |    |           |
|----------------------------------------|---------|----------------------|-----------|----|-----------|----|-----------|
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|                                        |         | CZ                   | 20004476  | EP | 1088113   | HU | 200102934 |
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|                                        |         | GB                   | 2376241   | WO | 200162994 | WO | 200162995 |
|                                        |         | WO                   | 200162996 | GB | 2362164   |    |           |

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ANNEX